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VOL. 19, SEC. A FEBRUARY, 1941 NUMBER 2

A NEW IONIZATION AMPLIFIER[1]

BY H. LE CAINE[2] AND J. H. WAGHORNE[3]

Abstract

A new type of instrument for measuring ionization currents is described. Whenever a charge is placed upon the electrode of the ionization chamber, an alternating voltage is obtained by electrostatic translation of the motion of a reed. The alternating voltage is amplified in an amplifier containing only standard radio parts and used to measure the ionization current by a condenser balance method. An instrument tested in the laboratory measured a quantity of 1.5×10^{-12} coulombs with about the same accuracy as a DuBridge and Brown instrument. The readings were recorded automatically and could be taken as rapidly as every three seconds with no linearity correction.

Introduction

In linear amplifiers used with an ionization chamber for measuring ionization currents, it is customary to connect the control grid of a tube directly to the electrode of the ionization chamber. A special tube is required in which the grid current from all sources has been reduced to the smallest practicable value. Such a tube is necessarily fragile and expensive. The associated circuit must be constructed with a view to obtaining the greatest stability possible. Circuits that provide a satisfactory degree of stability are cumbersome and are not ideally suited for further amplification of the output to permit the use of rugged recording mechanisms.

If the principle of the generating voltmeter is applied to convert the d-c. signal into an alternating voltage before amplification, important improvements in the operating characteristics of the circuit are obtained. The basic circuit is shown in Fig. 1. When a small quantity of charge is added to the system at A, the steady state conditions at B are unaltered as long as C_1 and C_2 are fixed. If either C_1 or C_2 is a periodic function of time, the alternating voltage appearing at B is changed by the addition of charge at A. The alternating voltage at B is proportional to the voltage at A and may be used to measure the voltage at A. Three points are of especial interest. The internal impedance of the device is inversely proportional to the modulation frequency and may be made sufficiently low that special precautions to raise the input resistance of the first tube are unnecessary. The fluctuations in

[1] *Manuscript received in original form September 9, 1940, and as revised, November 7, 1940. Contribution from the Department of Physics, Queen's University, Kingston, Ont.*

[2] *Holder of a Studentship under the National Research Council of Canada.*

[3] *At the time, holder of a Bursary under the National Research Council of Canada. Present address, National Research Laboratories, Ottawa.*

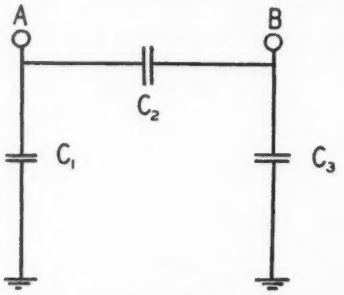

FIG. 1. *Generating voltmeter.*

output arising in the amplifier itself are now due to a band of frequencies from which the low frequencies may be excluded. For fairly narrow band widths, the random voltage is inversely proportional to the band width and has a lower limit depending upon the rapidity of action required of the device. The great decrease in noise level obtainable when a restricted frequency response may be introduced into a system has been widely used elsewhere. Finally, the usual values of input tube and ionization chamber capacity are such that it is not difficult to give to C_1 or C_2 values that result in a reasonable fraction of the maximum voltage obtainable. The maximum peak voltage is half the direct voltage developed at the input of a direct coupled amplifier when the input capacity is the same in both cases.

The principle of electrostatic translation has been used for some years in microphones, musical instruments, and voltmeters for measuring high voltages. In 1932 Hull (2) suggested the use of a vibrating reed as one electrode of a condenser for modulating a small direct voltage, but apparently the idea was not used. In the same year Gunn (1) and Kirkpatrick (3) published articles of a somehwat similar nature.

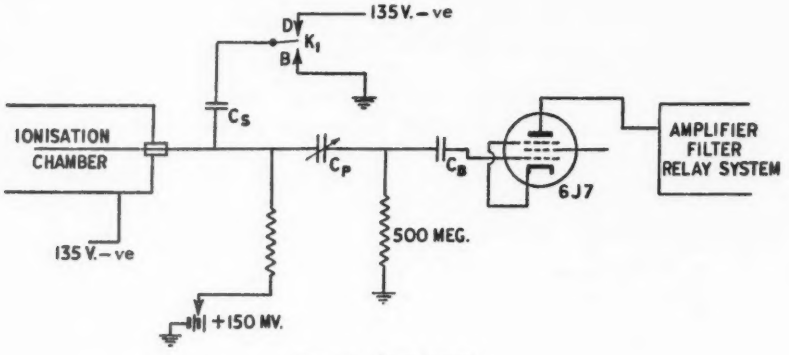

FIG. 2. *Input circuit.*

Experimental Amplifier

Fig. 2 shows an instrument tested in this laboratory. The ionization chamber electrode is connected directly to a stationary plate of a small air condenser C_p; the other plate of the condenser is a steel reed set vibrating at 120 cycle.sec^{-1} by means of an electromagnet supplied with 60 cycle current. The reed is tuned to 120 cycles by adjusting its length. The spacing between the reed and the stationary plate is only about 1/32 in., and the amplitude of vibration is of the same order. The cushioning effect of the air between the two surfaces of the condenser serves as an effective amplitude control for the reed. The reed is connected through a 500 megohm resistor to ground.

A circuit diagram including the amplifier is given in Fig. 3.

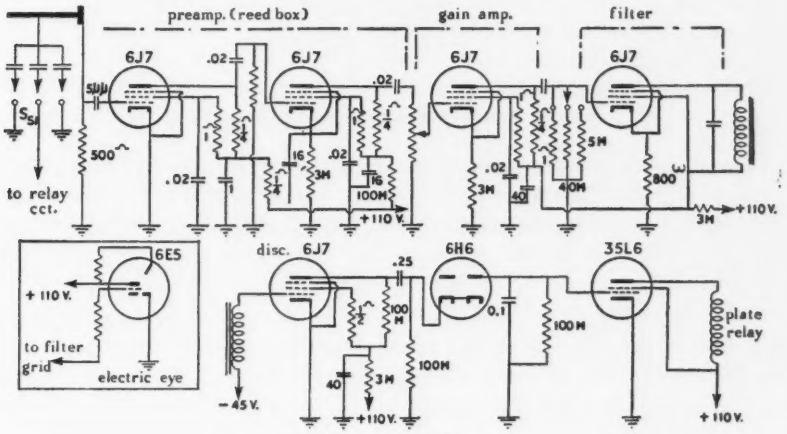

FIG. 3. *Amplifier.*

The mechanical construction of the periodic condenser and electrode system is shown in Fig. 4. The parts indicated are:—

A—cylinder that forms the outer electrode of one of the balance condensers;

B—condenser. The capacity between B and electrode is adjusted to be $\frac{1}{10}$ that between cylinder A to electrode.

C—not used (permanently grounded);

D—condenser. The capacity between *D* and electrode is adjusted to be $\frac{1}{100}$ that between A and electrode.

E—grounding key solenoid;

F—coil supplying a-c. energy to reed;

G—end of the electrode facing reed—$\frac{5}{8}$ in. diameter, faced with the same steel used in the reed;

H—reed of $\frac{5}{8}$ in. clock spring;

L—condenser composed of $\frac{1}{32}$ in. ebonite next to the reed and $\frac{1}{32}$ in. brass;

M—bracket for supporting two 6J7 tubes of preamplifier.

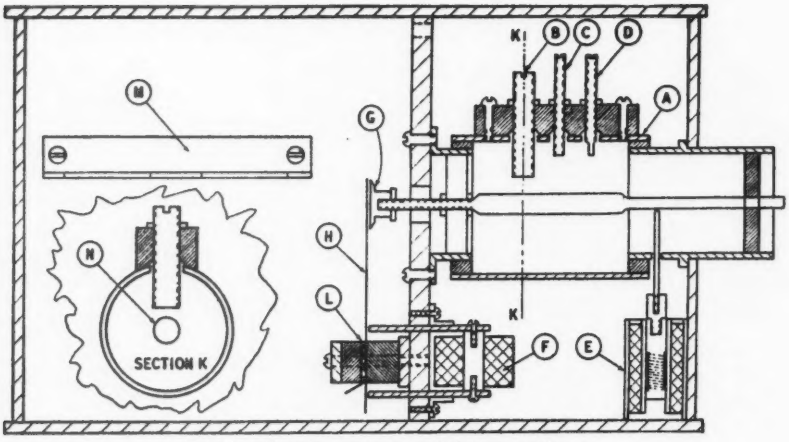

FIG. 4. *Periodic condenser and balance condenser.*

This unit, which is approximately 2 by 6 by 9 in., is connected to a second unit of approximately 6 by 9 by 12 in. by means of a flexible cable. The second unit contains the remainder of the amplifying and timing circuit together with four 45 volt portable *B* batteries used to provide standard voltages and a polarisizing voltage for the ionization chamber.

The relay system used is shown in Fig. 5. L_1 represents the plate relay coil, and S_1 the contacts on this relay. Contacts marked S_2 are controlled by the coil L_2. A bond indicates the position taken by a set of contacts when the corresponding coil is not energized.

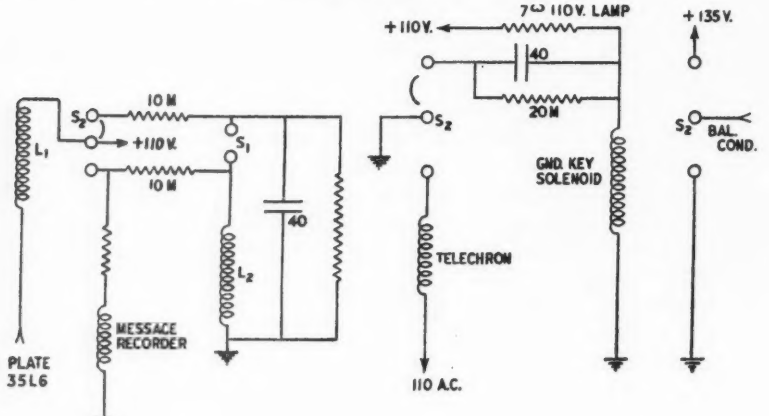

FIG. 5. *Circuit controlling the sequence of operations during a reading.*

The system is used as an electrometer, and currents are obtained by a modified balance method. The electrode voltage over a complete cycle is shown in Fig. 6. With K_1 in position D (Fig. 2) a polarizing voltage is set on the grounding key which is then released giving a signal of amplitude M. Owing to the flow of current in the ionization chamber the signal decreases to a minimum value A and the relay system operates to start a telechron timer and to switch K_1 to the position B, so that a definite charge is added to the electrode system, thus increasing the signal to the value P. Since the volt-ampere characteristic of the electrode system is linear, it is permissible to add all the balancing charge at once. The signal again decreases to the value A, at which time the relay system operates to stop the telechron, return K_1 to D and reconnect the grounding key momentarily, so that a new cycle is started automatically. A message recorder is connected to record the number of readings taken. The time measured by the telechron is the time required for the chamber electrode to collect a known charge, and enables the average current to be calculated.

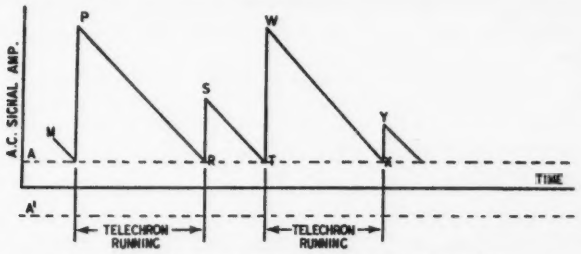

FIG. 6. *Variation of electrode voltage over two readings.*

Characteristics of the Device

The limit to the useful sensitivity is at present set by the insulation of the supports for the electrode assembly. The inclusion of the two 6J7 amplifier tubes in the same case as the reed assembly has proved unfortunate as it has been established that the temperature rise thus produced has a pronounced effect on this insulation. Sulphur has been found superior to ebonite in this respect.

An improvement in the timing circuit would result if the change of phase of the signal as it passes through zero amplitude were used to operate the relay system. It would then be impossible for the signal to pass through its minimum value too rapidly to allow the relay contacts to close. In a model tested, one side of the periodic capacity was grounded. A second stationary electrode was placed on the opposite side of the reed to the one already in use and a constant d-c. potential applied to it through a resistor. the a-c. signal produced was used as a standard with which to compare the phase of the original signal.

The instrument as constructed has a sensitivity range of 10^4 and requires about 1.5×10^{-12} coulombs for a full scale deflection. It will take readings every three seconds with no linearity correction. It should find application wherever a sensitive and rugged d-c. amplifier of very high input impedance is required. Small currents such as those arising in dielectric material may be observed under the most favourable conditions because the electrode assembly may be made as large or as small as desired. Surface conditions of the electrode faces of the periodic condenser had a pronounced effect on the polarizing voltage required for zero signal. This suggests a possible use in the study of surface voltages.

Acknowledgments

The writers would like to thank Dr. J. A. Gray and Dr. J. S. Marshall for their helpful interest in this work.

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NEW ELECTRONIC TRANSITIONS OF THE BH MOLECULE[1]

By A. E. Douglas[2]

Abstract

In a discharge in helium with a trace of boron trichloride and hydrogen three new bands are found at 3415 Å, 3396 Å, and 3099 Å. Measurements of these bands show that they are due to two new electronic transitions of the BH molecule. The upper states of both transitions are previously unknown $^1\Sigma^+$ states. The lower state of both transitions is the same and is a known $^1\Pi$ state. The rotational constants of both new states have been determined and their electron configuration is suggested.

Introduction

The spectrum of the BH molecule has been studied by several investigators. A complete record of all the known bands can be found in the papers of Thunberg (6) and of Almy and Horsfall (1). The only singlet band system of the BH molecule recorded by these investigators occurs around 4330 Å and is due to a $^1\Pi - {}^1\Sigma^+$ transition. The $^1\Sigma^+$ state is the ground state of the molecule. In what follows, the observation and analysis of three new singlet bands of BH, which involve two new electronic states, will be described.

Experimental

The spectrum was excited in an uncondensed discharge through a tube of the type described by Douglas and Herzberg in a previous paper (2). The tube was filled with helium to about 15 mm. pressure and sufficient hydrogen was added that H_α and the adjacent red helium line had about the same intensity. This is an extremely small amount of hydrogen, and usually the hydrogen occurring as an impurity in the tube was sufficient. To this mixture a small amount of boron trichloride was added and the discharge tube was then operated in the manner described in the previous paper (2).

Under these conditions the well known BH band at 4330 Å appeared with an intensity so great that it could be photographed in the third order of the 21 ft. grating spectrograph in a few minutes. At the same time three new, much weaker bands, which had their Q heads at 3415 Å, 3396 Å, and 3099 Å, were observed. They were photographed in the second order of the grating spectrograph with a dispersion of about 1.4 Å/mm. The exposure time was about 20 min. The wide structure of the bands indicated immediately that they are hydride bands, and the analysis confirms the assumption (suggested by the conditions of excitation) that they are due to BH.

[1] *Manuscript received November 16, 1940.*

Contribution from the Department of Physics, University of Saskatchewan, Saskatoon, Sask., with financial assistance from the National Research Council of Canada.

[2] *At the time graduate student, holder of a Bursary (1939–1940) under the National Research Council of Canada. At present at the University of Minnesota.*

Analysis of the Bands at 3415Å and 3396Å

The two bands at 3415 and 3396 Å, which obviously belong together, were relatively free from other overlapping bands (BCl, AlCl, etc.) and could therefore be accurately measured. Each of them consists of a P, a Q, and an R branch. In consequence of the open structure of the bands the branches could be picked out and the quantum numbers assigned by inspection.

The first three columns of Table I show the wave numbers of the lines in the band at 3415 Å (0−0 band). Though lines due to the $B^{10}H$ molecule could be seen they were not measured. All lines are single, showing that the band represents a singlet transition. Since the first line of the P branch $P(1)$ is present and the first line of the R branch $R(0)$ is missing, the bands must be due to a $^1\Sigma - {}^1\Pi$ transition. The fourth column of Table I gives the values

TABLE I

WAVE NUMBERS OF THE LINES AND COMBINATION DIFFERENCES IN THE BH BAND AT 3415 Å (0−0 BAND OF $^1\Sigma^+ - {}^1\Pi$ SYSTEM)

$\nu_0 = 29272.78$ cm.$^{-1}$

J	$R(J)$	$Q(J)$	$P(J)$	$\Delta_2F''(J) = R(J-1) - P(J+1)$	$\Delta_2F'(J)$ for band 4330 Å after Thunberg
0					
1	29321.44	29273.24	29248.89		
2	346.21	74.05	225.49	119.02	119.10
3	371.09	75.22	202.42	166.46	166.34
4	396.31	76.86	179.75	213.51	213.54
5	421.68	78.88	157.58	260.39	260.37
6	447.19	81.32	135.92	306.85	306.76
7	472.92	84.26	114.83	352.82	352.79
8	498.80	87.68	094.37	398.33	398.31
9	524.83	91.60	074.59	443.19	443.02
10	551.03	96.01	055.61	487.42	487.45
11		29301.00	037.41	530.88	531.01
12		06.56	020.04		
13		12.73			
14					

of $\Delta_2F''(J) = R(J-1) - P(J+1)$ calculated from the measurements of the new band, while the fifth column gives the values of $\Delta_2F'(J) = R(J) - P(J)$ calculated from the data given by Thunberg for the 0−0 band of the $^1\Pi - {}^1\Sigma$ transition of BH. The agreement of corresponding values in the two columns shows definitely that the two electronic transitions have the $^1\Pi$ state in common. The good agreement also establishes the fact that the upper state for the new bands is a $^1\Sigma^+$ state. If it were a $^1\Sigma^-$ state the Λ type doubling of the $^1\Pi$ state would prevent such an agreement.

In Table II are given the wave numbers of the lines in the band at 3396 Å. It can be shown by means of the agreement of the combination differences that the lower state for this band is the upper state for the 1−1 band of the $^1\Pi - {}^1\Sigma$ system around 4330 Å. This establishes the fact that the bands at 3415 Å and 3396 Å are the 0−0 and 1−1 bands of the same system.

Since only the 0−0 and 1−1 bands have been observed, the vibrational constants of the new $^1\Sigma^+$ state can not be determined directly. A rough value can be obtained by using the formulae $\omega_e^2 = \frac{4B_e^3}{D_e}$ and $\omega_e x_e = \frac{0.7\alpha\omega_e}{B_e}$ [see (6)]. The vibrational constants so determined are listed together with the rotational constants for the new state in Table III. Since the constants for the $^1\Pi$ state have been determined by several investigators they have not been evaluated from the new data. The agreement of the values of $\Delta_2 F(J)$ for the $^1\Pi$ state calculated from the present data and from the data given by Thunberg shows that any re-evaluation of the constants would not lead to a significant change.

TABLE II

WAVE NUMBERS OF THE LINES OF THE BH BAND AT 3396 Å
(1−1 BAND OF $^1\Sigma-^1\Pi$ SYSTEM)

$\nu_0 = 29433.75$ cm.$^{-1}$

J	$R(J)$	$Q(J)$	$P(J)$
0	—	—	—
1	29480.59	29434.71	29411.57
2	504.86	36.10	389.95
3	529.62	38.33	368.98
4	555.03	41.25	348.84
5	581.01	44.90	329.48
6	607.48	49.43	310.98
7	634.42	54.76	293.58
8	661.72	60.94	Covered
9		68.08	261.90
10		76.24	247.89
11		85.40	235.19
12		95.79	223.99
13			214.35

TABLE III

CONSTANTS FOR THE UPPER $^1\Sigma$ STATE OF THE BANDS AROUND 3415 Å

B_0, cm.$^{-1}$	B_1, cm.$^{-1}$	α, cm.$^{-1}$	B_e, cm.$^{-1}$	$r_e 10^{-8}$cm.	D_e, cm.$^{-1}$	ω_e, cm.$^{-1}$	$\omega_e x_e$, cm.$^{-1}$
12.083	11.512	0.571	12.368	1.215	0.00134	2400	65

Analysis of the Band at 3099 Å

The BH band at 3099 Å has a structure very similar to the one at 3415 Å, but it is not as intense. Since a strong group of aluminium atomic lines falls on this band, a discharge tube with iron electrodes had to be used. Though this removed the troublesome aluminium lines the BH band was still overlapped by a band of SiCl, which was obviously formed by the action of the active chlorine (formed by the decomposition of boron trichloride in the discharge) on the glass walls. Owing to the small intensity and the overlapping SiCl band only the P and Q branches of the BH band at 3099Å

could be measured. The wave numbers of the measured lines are given in Table IV.

TABLE IV

WAVE NUMBERS OF THE LINES AND COMBINATION DIFFERENCES IN THE BH BANDS AT 3099 Å

$\nu_0 = 32260.04$ cm.$^{-1}$

J	$P(J)$	$Q(J)$	$\Delta_1F'(J)$
0			24.57
1	32235.88	32260.52	48.83
2	212.66	61.69	73.15
3	189.98	63.53	97.32
4	168.07	66.06	121.62
5	146.60	69.23	145.55
6	126.15	73.11	169.26
7	106.55	77.69	192.74
8	087.74	82.91	216.18
9	069.84	89.05	
10		96.03	

Since the first line of the P branch is present in this band the upper state is also a $^1\Sigma^+$ state. It is found that the values of $Q(J) - P(J+1)$ calculated from the measurements of this band are equal to the values of $R(J) - Q(J)$ calculated from Thunberg's data for the 0—0 band of the $^1\Pi - {}^1\Sigma^+$ transition at 4330 Å. The lower state for the new band must therefore be the known $^1\Pi$ state, just as for the bands 3415 and 3396 Å. The agreement also establishes the fact that the upper state is $^1\Sigma^+$, not a $^1\Sigma^-$ state.

In order to obtain the constants for the $^1\Sigma^+$ state, $\Delta_1F'(J)$ was calculated by subtracting the Λ doubling of the $J+1$ level of the $^1\Pi$ state from the value of $Q(J+1) - P(J+1)$ calculated from the new band. The Λ doubling of the $^1\Pi$ state was taken from Thunberg's data. The values of $\Delta_1F'(J)$ are shown in the last column of Table IV. The constants of the upper state of the new band are found to be:

$$B_0 = 12.23 \text{ cm.}^{-1}, \quad D_0 = 0.00148 \text{ cm.}^{-1}, \quad r_0 = 1.222 \cdot 10^{-8} \text{ cm.},$$

$$\omega_0 = \sqrt{\frac{4B_0^3}{D_0}} = 2230 \text{ cm.}^{-1}.$$

Electronic Structure of the BH Molecule

In Table V the known electronic states of AlH and BH are compared. The data for AlH are from Sponer (5, vol. 1). It is interesting to note that with the two new $^1\Sigma^+$ states of BH found here there is a complete analogy between the electronic states of BH and AlH.

The six electronic states of BH can easily be accounted for by the following four electron configurations:

$(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2$	$^1\Sigma^+$
$(1s\sigma)^2(2s\sigma)^2 2p\sigma 2p\pi$	$^3\Pi$ $^1\Pi$
$(1s\sigma)^2(2s\sigma)^2(2p\pi)^2$	$^3\Sigma^-$ $^1\Sigma^+(^1\Delta)$
$(1s\sigma)^2 2s\sigma 2p\sigma(2p\pi)^2$	$^1\Sigma^+(^1\Delta\ ^3\Sigma^-\ ^5\Sigma^-\ ^3\Sigma^-\ ^1\Sigma^-\ ^3\Delta\ ^3\Sigma^+)$

TABLE V

EXCITATION ENERGIES OF THE KNOWN ELECTRONIC STATES OF BH AND AlH

State	Excitation energy	
	BH	AlH
$A^1\Sigma^+$	0	0
$a^3\Pi$	x	y
$B^1\Pi$	23073.8	23470.9
$b^3\Sigma$	$x + 27056.7$	$y + 26100$
$C^1\Sigma^+$	52346.6	44597.1
$D^1\Sigma^+$	55333.6	49288

While the first two have been assumed previously to account for the two lowest singlet states (5, vol. 1) the two others seem to be the most likely configurations for the newly found states (as well as for the $^3\Sigma$ state). It is probable that the electron configurations for the corresponding states of AlH may be obtained simply by changing the principal quantum number 2 to 3 and adding the complete L shell of Al. However, one difficulty is that the observed transitions $C^1\Sigma^+ \rightarrow A^1\Sigma^+$ and $D^1\Sigma^+ \rightarrow A^1\Sigma^+$ of AlH (not observed for BH) would involve simultaneous jumps of two electrons.

Acknowledgments

This investigation was made possible by a grant from the Penrose Fund of the American Philosophical Society and also a grant for research to Professor Herzberg from the National Research Council of Canada. Finally the author is greatly indebted to Dr. G. Herzberg for giving much valuable advice and help during the course of this work.

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THE REDUCTION OF RESAZURIN IN MILK AND AQUEOUS SOLUTIONS[1]

BY H. R. THORNTON[2], F. MCCLURE[3], AND R. B. SANDIN[4]

Abstract

The action of resazurin in milk is complex and not as yet clearly understood. The various resazurin tests have been proposed as practical tests for estimating bacterial populations in milk before they have emerged from the experimental stage. A significant proportion of results cannot at present be interpreted with the reasonable certainty necessary to justify widespread use of these tests by the dairy industry.

The colour changes undergone by resazurin in milk have been proposed over a period of eleven years as the basis for a test, or number of tests, to supplant the methylene blue reduction test as a measure of bacterial populations in raw milks. Yet Johns and Howson (13) are the first to publish E_h-time curves of resazurin. Their work serves to bring into sharp focus some of the exaggerated claims for resazurin, particularly for the one-hour test.

The purpose of the present communication is to set forth further and confirmatory evidence and to evaluate some of the proposed resazurin tests in the light of that evidence.

Methods

For the E_h measurements in milk, 0.1 ml. of a 0.05% solution of resazurin was added to 10 ml. of milk. Three preparations of resazurin, two American* and one European, were studied. The new standard methylene blue thiocyanate tablets were used, resulting in a concentration of 1 part of dye to 300,000 parts of milk. Oxidation-reduction potentials were measured by means of the usual electrometric set-up, the potentiometer** being a Leeds and Northrup type K2.

[1] *Manuscript received August 19, 1940.*

Contribution from the Departments of Dairying and Chemistry, University of Alberta, Edmonton, Alta.

[2] *Professor of Dairying.*

[3] *Graduate Student in Chemistry.*

[4] *Associate Professor of Chemistry.*

* *The American resazurin was manufactured by The National Anilin and Chemical Co. Part of the dye was supplied through the courtesy of this company and Dr. H. J. Conn, Chairman, Commission on Standardization of Biological Stains. It is not known whether the two samples were from the same dye batch.*

** *The potentiometer was purchased with funds obtained from the National Research Council of Canada, Ottawa.*

Preliminary Chemical Studies

The available information regarding the chemistry of resazurin is very meagre, indeed (see Neitzki *et al.* (15).). Gunderson and Templeton (8), on treating an aqueous solution of resazurin with carbon dioxide, obtained a purple-black precipitate and a red supernatant liquid. When the precipitate was dissolved in dilute alkali, "the resulting blue solution behaved in the normal manner". On the concentration of the supernatant red liquid with simultaneous removal of the carbon dioxide, a reddish-blue solution was obtained which was thought to be resazurin. The addition of carbon dioxide to milk accelerated the first colour change of added resazurin.

It is common experience that some samples of commercial resazurin are unfit for use in a reduction test in milk. Manufacturers report to the writers that resazurin is a difficult chemical to prepare, that large and varying quantities of resorufin are synthesized along with the resazurin, attempts to remove which are probably not wholly successful, and that another substance of unknown constitution is thought to be synthesized during the manufacture of the resazurin.

In a preliminary study of the chemistry of resazurin the present authors were unable to obtain a titration curve with the European dye in aqueous solution. The American dye gave a perfect two-step titration curve at approximately pH 1, and dye reduction was completely reversible at this pH. At pH 7 reproducible potentials were unobtainable, decomposition of the dye presumably having taken place, and reversibility of reduction was not complete. Preliminary attempts to purify the dye or to synthesize resazurin in a pure state failed. Although more extensive trials might prove successful, the experiments indicate that considerably more information on the chemistry of resazurin is necessary before satisfactory standards for a reduction test in milk can be evolved.

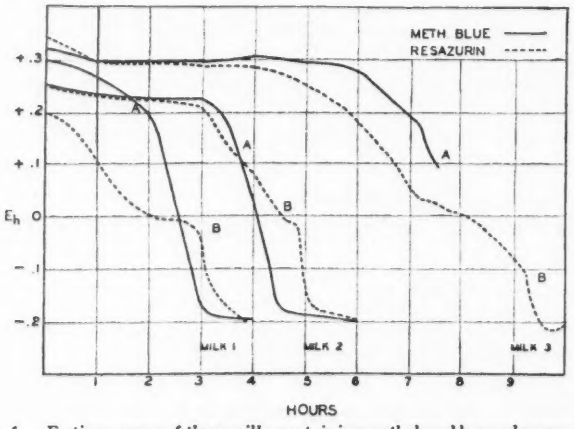

FIG. 1. *E_h-time curves of three milks containing methylene blue and resazurin.*

The Reduction of Resazurin in Milk

In Fig. 1 are shown E_h-time curves of methylene blue and resazurin milk mixtures for three samples of milk. The methylene blue milks had reduced at the points marked *A*, while the resazurin tubes were white at the points marked *B*. In the methylene blue tube of Milk 3 the electrode was inadvertently broken shortly after reduction of the dye but the essential part of the curve is not affected. It is included here because Milk 1 is Milk 3 after 24 hours' incubation at room temperature, unincubated milks of high bacterial content not being available in this city. There is a good deal of similarity between these curves and those reported by Johns and Howson.

It will be noted that the resazurin curves followed the methylene blue curves for the first two to three hours in Milks 2 and 3. Then the resazurin milks became measurably negatively poised until reduction to the white compound had taken place, when the poising effect was lost. In Milk 1, in which the inherent poising capacity of the milk was largely decreased by bacterial action, the milk was immediately overpoised by the resazurin. It is apparent from these curves that the red-white reaction, or a component of it, strongly poised the milk electronegatively, the overpoising effect becoming apparent as the initial poising of the milk was lessened through bacterial action. Therefore, the time required to reach either the pink or white end-point was a function not only of bacterial influences but also of the comparative poising capacities of the milk and dye systems.

Vat milk from a pasteurizing plant was used for this work because it was thought likely to be more uniform and less subject to irregularities than individual milks. Notwithstanding this precaution an interesting exception was observed and Fig. 2 is presented because it represents a time-potential curve of methylene blue in milk which deviates materially from the classical shape

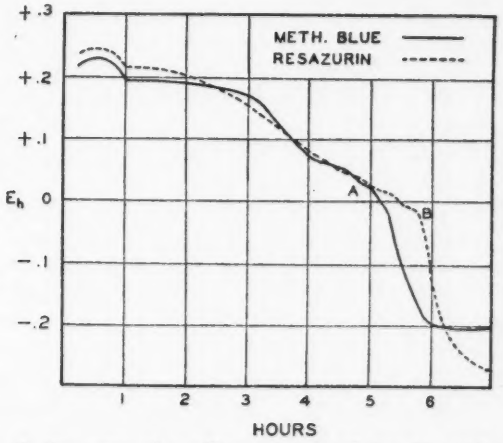

FIG. 2. *E_h-time curves of a milk containing methylene blue and resazurin.*

of curve as represented in Fig. 1. The milk used for the two dye milk mixtures was a vat sample that was discovered to have been run through a centrifugal clarifier. Suspecting that clarification might account for the unusual shape of the methylene blue milk curve, samples of a mixed vat milk before and after clarification were mixed with methylene blue in standard concentration and the potential changes followed as shown in Fig. 3. There is no evidence that clarification influenced the poising properties of this milk. Therefore, no explanation is attempted for the unusual results with the milk used for Fig. 2.

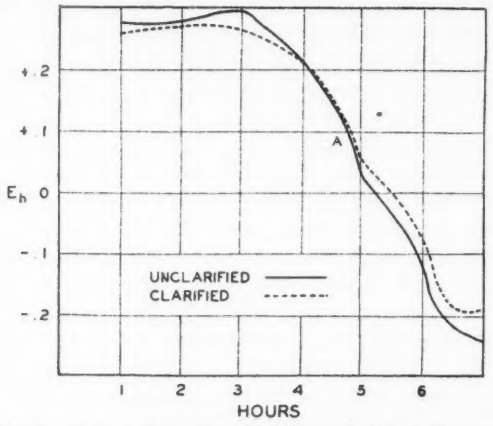

FIG. 3. *E_h-time curves of a milk before and after clarification.*

All attempts to reproduce the blue colour in milk by oxidation of the reduced resazurin failed. It would appear that the reduction of resazurin in milk is not a reversible reaction. The strong poising influence of the red-white reaction and its loss on complete reduction shows that at least one step in the reducing process is reversible.

The Pink End-point Test

The original resazurin test proposed by Pesch and Simmert (17) carried reduction only to the pink end-point. This first step in the reduction of resazurin is thought to be irreversible, and, in consequence, the test was believed by these authors to be insensitive to the presence of dissolved oxygen, janus green being cited as another such insensitive dye. Thornton and Hastings (19) pointed out the error of this assumption in regard to janus green B and the same reasoning holds for resazurin, a view substantiated by the recent interesting Vermont bulletin (6).

Collins *et al.* (2) and Johns (11) favour the resazurin-to-pink test, the advantage claimed being that the pink end-point is reached before methylene blue is reduced and time is thereby saved. To off-set this, however, it should be recognized that this end-point is subject to the same disadvantage as was

found in the case of janus green B by Thornton and Hastings, i.e., indefiniteness caused by (i) a mixing of the colours blue, red, and white, and (ii) the acceleration or retardation of E_h changes in milk overpoised by the red-white reaction. No exact and reproducible colour standard for determining this end-point has as yet been proposed, but the use of such a standard would not compensate for the differences in the slopes of the E_h-time curves of different milks. A further complicating factor is the colour sensitivity of resazurin to H-ion concentration, even yellow being reported as one of the possible colours.

Anomalies

When working with resazurin one quickly observes puzzling anomalies. Thus in the present study the colour changes were not always consistent at different temperatures; the extreme sensitivity to light reported by others was not observed by the writers; some milks with long methylene blue reduction times reduced resazurin quickly, and for this there was no apparent explanation; it was not unusual for the pink colour to remain in some milks for a surprisingly long time; the European sample of resazurin did not give the usual colour when added to milk and was unsatisfactory as an E_h indicator for this test.

Johns (12), Nelson (16), and Davis (4) report that some samples of resazurin are unsatisfactory as indicators in a reduction test. Keenan *et al.* (14) found that, of 200 milks reducing methylene blue in not less than five hours, 6% reduced resazurin to the white compound in not more than one hour and more than 50% of 163 samples which were vivid pink in the resazurin test at the end of one hour did not reduce methylene blue in less than five hours. Davies *et al.* (3) found that 11% of the samples reducing resazurin to purple pink in one hour failed to reduce methylene blue in seven hours. Some of Frayer's (6) resazurin-to-white reduction times were shorter than the methylene blue reduction times.

According to Collins *et al.* the reduction of resazurin to pink requires an average of 50% of the methylene blue reduction time. Johns and Howson on the other hand obtained a ratio of 3 : 4 between the resazurin-to-pink and methylene blue average reduction times. They attribute this discrepancy to their own use of the shaking technique or to end-point differences. Since Johns and Howson used the modified technique with both dyes and Collins *et al.* used the standard technique with both dyes, this difference in procedures remains an inadequate explanation. Difficulties of end-point determination are serious in any of the reduction tests and are particularly impressive to an operator using the resazurin pink end-point.

Any attempted explanation of these anomalies at the present time would constitute mere conjecture. However, the possibilities of the overpoising effects and decomposition of resazurin in some milks would seem to deserve further attention if this test is to be used in practice.

Shortening the Reduction Time

Clark, Cohen, and Gibbs (1) expressed the desirability of shortening the time of the methylene blue reduction test. Thornton and Hastings recognized some of the difficulties in such shortening. Ramsdell *et al.* (18) criticized the view expressed by Thornton and Hastings, considering that the behaviour of resazurin in milk justifies the assumption of a sound and interpretable decrease of reduction time. Johns (personal communication) believes that "the shortening of the reduction time is due chiefly to the poising effect of resazurin coming into play after the original poising of the milk has been partially overcome by bacterial growth." Davis (4) stated that, because resazurin is electropositive to methylene blue and both are electronegative to fresh milk, "It will be evident, therefore, that very weak reducing systems in milk, irrespective of their nature of origin, will affect resazurin much more than methylene blue." The same view was earlier expressed by Ramsdell *et al.* The E_h curves of Johns and Howson and those contained herein do not bear out this contention and show that the difference in the E_o values of the two dyes exerts but slight, if any, influence on reduction times, the time saved in the resazurin test being largely the result of the overpoising effect of the red-white reaction.

The possibility of shortening the reduction test by overpoising the milk with a dye system was suggested to one of the present authors (T) fifteen years ago by Dr. Barnett Cohen. According to present theories this appears to be feasible only if milks do not vary in their inherent reducing intensities and capacities. Hobbs (9) considered that milks do not vary in reducing capacities (poising). On the other hand, Greenbank (7) contended that milks do so vary and presented good evidence in substantiation of his contention. The variation in reducing intensity of different milks is too well known to require comment. Some abnormal milks, such as many mastitis milks, behave in a manner very suggestive, indeed, of enhanced poising properties. Since market milks are dilutions of abnormal with normal milks, it is not unreasonable at present to assume varying poising in market milks. Until more is known of the nature of poising inherent in milk, interpretations of the behavior in milk of such strongly poised systems as resazurin should be tempered with caution.

Another possible mechanism for shortening the reduction test is the removal of a portion of the dissolved oxygen from the milk by non-poised chemical agents, leaving less oxygen for bacterial consumption. This procedure depends on the generally accepted theory that the bacteria play an oxygen-consuming role in the reduction test. This theory has recently been questioned by Hobbs (9) who found no relation between the time of reduction of methylene blue in milk by pure cultures of certain bacteria and their rate of oxygen consumption in the Barcroft apparatus. Miss Hobbs' belief does not find apparent substantiation in the common and simple observation that shaking a reduced tube of milk with oxygen oxidizes the methylene white, or that evacuation of the tube shortens the reduction time. Neither does it permit interpretation

of Jackson's findings (10) that exposure of anaerobically drawn milk to minute amounts of atmosphere immediately poises the milk at the usual E_h levels of fresh aerobically drawn milk. It may be that the rate of oxygen fixation by bacteria in a moving vessel partly filled with milk is not necessarily representative of oxygen removal from unagitated milk sealed by a butterfat layer. The more recently advanced evidence of Frayer (6) leaves little doubt that the reduction of dyes and the oxygen content of the milk are intimately related. However, the development of a reduction test shortened by the partial removal of oxygen by non-poised chemical agents is at present attended by difficulties and is a matter for the future.

Discussion

When a reversibly reducible system, such as methylene blue, is added to milk, the milk dye mixture comes to an E_h equilibrium at which point the dye exists partly in the oxidized and partly in the reduced form. The proportion of the two forms present is a function of the E_h value of the equilibrium. There are reasons for believing that milks differ in the initial E_h value at which they are poised and in the E_h value of the equilibrium they attain with an added dye system. There is evidence (10) indicative of lapsed time before such an equilibrium is reached in fresh milk of low bacterial content, and that this time factor may be an hour or even longer. Thus, when methylene blue is added to milks variable proportions of the dye change in variable periods of time to methylene white. This phenomenon escapes notice because the reductant is colourless.

It is probable that the one-hour resazurin test, when applied to normal milk of low bacterial content, merely measures the E_h value of the equilibrium reached by the milk dye mixture in one hour, since the oxidant in this case is blue while the reductants are red and colourless. This situation is made even more extreme by the strong poising action of the red-white reaction. Such a view receives support, not only in the general poor correlation between the resazurin and methylene blue tests as found by Frayer (5), but also in the data presented by Ramsdell *et al.* (18). Fig. 4 is a scatter-graph prepared by the present authors from the one-hour resazurin numbers and the methylene blue reduction times of 78 milks reported by Ramsdell *et al.* The lack of correlation, especially in the case of the good milks, is quite apparent.

Thornton and Hastings drew attention to the difficulty of interpreting milk reduction of indicators more electropositive than methylene blue, and the startling recent claims for the one-hour resazurin test seem to justify their view. Ramsdell *et al.* consider that the reduction even of methylene blue may be misleading because visual reduction in some milks may be effected at E_h levels as positive as the initial values of other milks. Attempts to explain the varying E_h ranges over which methylene blue reduces in milk have not been entirely satisfactory. Since methylene blue reduces in milk after bacterial action has assumed control of the E_h, i.e., after the potential has attained

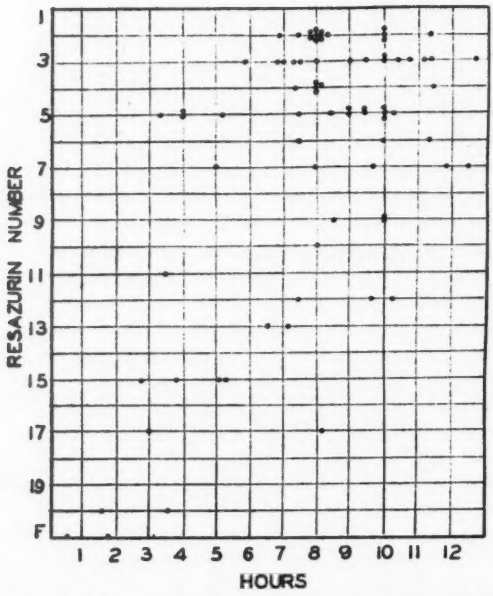

FIG. 4. *Scattergraph of the one-hour resazurin numbers and the methylene blue reduction times of 78 milks reported by Ramsdell et al.*

a steady negative drift and the upper break in the potential-time curve is discernible, it is probable that the reduction of methylene blue is not misleading in the manner suggested by Ramsdell *et al.*

The writers have seen no evidence, either in the literature or in their own experiments, that the resazurin test is sensitive to bacterial action during the first hour of incubation of a normal milk of low bacterial content. They are not acquainted with any theory that opens the possibility of a redox indicator being more sensitive to bacterial action than the O-R potential itself. On the other hand, when the bacteria begins to influence the O-R potential of the milk, resazurin may indicate the potential change more quickly than will methylene blue. This is illustrated in Fig. 1, Milk 1. Therefore, the one-hour resazurin test shows promise in indicating milks that will reduce methylene blue in periods up to about two hours.

The one-hour resazurin test seems to permit the separation of milks into two classes—those of very high bacterial content and those of low bacterial content. This picture, however, is complicated by the fact that some milks of low bacterial content, presumably abnormal, are rather strongly poised at E_h levels negative to the usual values of fresh milk. The one-hour resazurin test of some of these milks would, therefore, be independent of bacterial

action and, as a strictly bacteriological test, difficult of interpretation. Again further possible complications arise because of the behaviour of resazurin as a pH indicator.

Conclusions

The following conclusions are drawn from a potentiometric study of the behaviour of resazurin in milk and aqueous solutions:—

1. A European preparation labelled resazurin did not behave in the expected manner, was probably not resazurin, and was unsuitable as an indicator of reduction in milk.

2. Resazurin exhibiting the frequently described colour changes in milk is a redox indicator, at least at pH1. At pH7 the evidence is not yet clear.

3. The chemistry involved in these changes is probably as yet undetermined.

4. The blue-red reaction is electropositive and the red-white reaction is electronegative to the methylene-blue–methylene-white reaction.

5. In long time reducing milks as measured by methylene blue, the resazurin time-potential curve follows the methylene blue curve for the first two to three hours. The mixture then becomes strongly poised by the red-white reaction, this poising influence being rather sharply lost when reduction to the white compound is complete.

6. In milks reducing methylene blue in periods up to two to three hours, the time-potential curve of resazurin resembles the later stages of the resazurin time-potential curve in good milk.

7. The colour attained at the end of one hour by resazurin in milk of low bacterial content depends on the E_A value of the equilibrium set up by the mixing of the reducing systems of the dye and milk, and no evidence was forthcoming that it is related to the number of bacteria in such milk.

8. The one-hour resazurin test shows some promise as a means of segregating milks that will reduce methylene blue in periods up to two to three hours, but is complicated by the strong poising influence of the red-white reaction.

9. Intelligent interpretation of the one-hour resazurin test was not found to be always possible in the present state of knowledge.

10. The authors believe that the resazurin test has been placed in the hands of the dairy industry before it has emerged sufficiently from the experimental stage.

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THERMAL STUDIES ON ASBESTOS

I. EFFECT OF TEMPERATURE AND TIME OF HEATING ON LOSS IN WEIGHT AND RESORPTION OF MOISTURE[1]

By D. Wolochow[2] and W. Harold White[3]

Abstract

Heating a chrysotile asbestos mill fibre has shown that in the approximate temperature range of 500 to 700° C. the loss in weight depends on both the time and temperature. At other temperatures the loss is practically independent of the time.

Prolonged heating at about 490° C. expelled about 25%, and at 510° C. about 50% of the combined water. Complete dehydration occurred on prolonged heating at about 580° C., but only above 700° C. was the loss in weight rapid.

On the basis of the data obtained on the resorption of moisture it is suggested that heating for half an hour at 215° C. would be a more accurate and rapid method for determining free moisture than that commonly employed.

Introduction

Previous published studies on the thermal treatment of asbestiform minerals have been limited to the effect of temperature on physical properties, such as tensile strength (4, 6) and the accompanying chemical changes (3, 5, 7, 9). The effect of time of heating has not been studied. The purpose of the present investigation was to obtain as complete information as possible on the effect of both temperature and time of heating on the loss in weight of chrysotile asbestos fibre, and on the subsequent sorption of moisture by the heated fibre.

Methods and Materials

A quantity of a Canadian mill fibre* (Quebec Standard Test: 1.7–9.3–4.0–1.0) was conditioned at 65% relative humidity and 70° F. Ten-gram samples were loosely packed into large crucibles and heated in an electric furnace with automatic temperature control (±8° C.), at temperatures up to 904° C. and for periods up to 20 hr. After heating, the samples were cooled in a desiccator and weighed. They were then replaced in the conditioning room, and the regain in weight, due to water resorption, determined.

Because of the importance of the time of heating between 493 to 555° C., heat treatments in this temperature range were made for periods up to almost 300 hr.

To determine the effect of repeated heating, a condition to which asbestos is exposed in normal use, loss determinations were made on one sample heated at all temperatures studied in this investigation.

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[2] *Chemist, Division of Chemistry.*

[3] *Biochemist, Food Storage and Transport Investigation, Division of Biology and Agriculture. Formerly, Chemist, Division of Chemistry.*

* *Percentage composition of the dry fibre (loss at 110° C. = 1.4%): SiO_2, 40.2; Al_2O_3, 3.4; FeO, 1.9; Fe_2O_3, 0.7; MgO, 40.3; CaO, 0.48; CO_2, 0.20; ignition loss, 13.3.*

TABLE I

PERCENTAGE LOSS IN WEIGHT ON HEATING SAMPLES OF CANADIAN CHRYSOTILE ASBESTOS (MILL FIBRE) AT VARIOUS TEMPERATURES AND PERIODS OF TIME

Temp. of heating, °C.	Period of heating, hr.				
	0.25	0.50	1	2	20
110	1.27	1.33	1.40	1.38	1.40
160		1.61	1.52	1.52	1.61
216	1.72	1.79	1.80	1.85	1.94
271	1.96	2.06	1.95	2.00	2.18
327	2.14	2.17	2.29	2.34	2.52
382	2.35	2.40	2.82	2.79	3.05
438	3.16	3.13	3.23	3.21	3.29
493	3.36	3.34	3.46	3.51	3.72
555	4.12	4.41	4.92	5.30	*10.15
582	4.45	4.81	5.17	8.16	*13.31
604	4.84	4.76	6.27	10.32	*13.50
632	6.21	7.67	11.15	13.27	14.00
671	8.87	12.93	13.89	14.00	14.14
704	13.18	13.99	14.21	14.22	14.28
804	14.42	14.45	14.54	14.60	14.83
904	14.66	14.75	14.79	14.60	14.86

	555	*582*	*604° C.*
** 6 hr.*	*7.8*	*10.1*	*13.1*

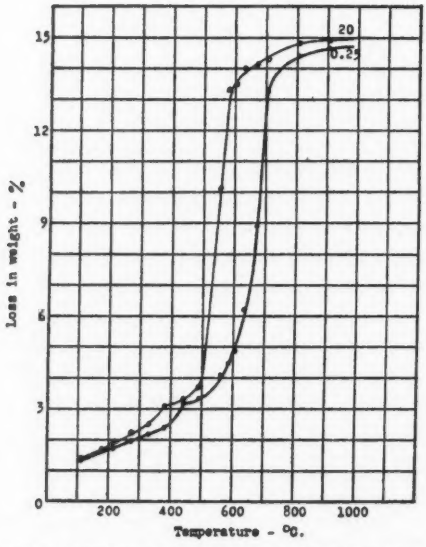

FIG. 1. *Weight lost by Canadian chrysotile asbestos (mill fibre) on heating for 0.25 hr. and 20 hr.*

Results and Discussion

The data obtained for the loss in weight after heating are given in Table I. In Fig. 1, the loss on heating for 0.25 hr. and 20 hr. has been plotted against the temperature of heating. From these it may be seen that, independently of the time of heating, a certain critical temperature must be reached before complete dehydration will occur. From Fig. 2, in which the loss at various temperatures has been plotted against time of heating, it is evident that at temperatures below 493° C. the loss in weight is practically independent of the time of heating. However, at temperatures between 493 and 704° C., the loss in weight is considerably affected by the time of heating, increasing markedly with increase of time. At and above the latter temperature the loss is again practically independent of the time of heating.

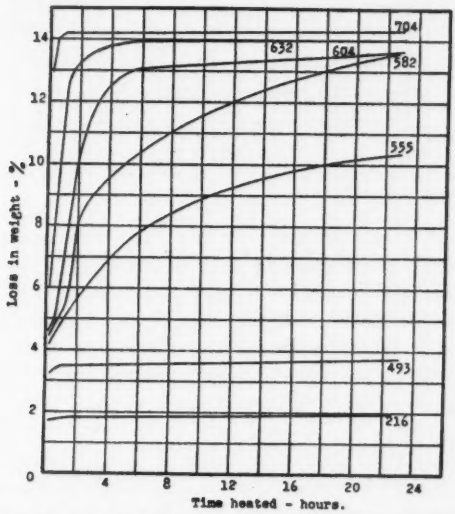

FIG. 2. *Weight lost by Canadian chrysotile asbestos (mill fibre) on heating at indicated temperatures (°C.).*

The data obtained from the more detailed examination of the effect of time and temperature of heating in the range 493 to 555° C. are graphically presented in Fig. 3. The points representing the loss in weight after heating for various time intervals at 510, 516, and 527° C. have been joined with broken lines because it is doubtful whether these are significant, except in so far as they indicate that in this temperature range the fibre is very sensitive to small changes in temperature. To definitely establish the course of dehydration in this temperature zone would require very precise control of temperature and other factors, over long periods of heating.

Taking into account the content of moisture, carbonates and ferrous iron, the maximum loss in weight of 4.8% at 493° C. corresponds approximately to

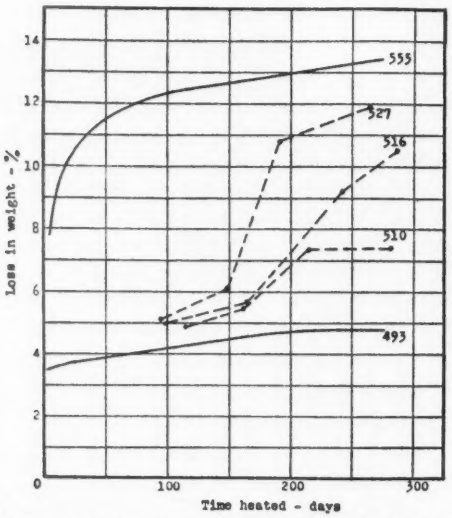

FIG. 3. *Weight lost by Canadian chrysotile asbestos (mill fibre) on prolonged heating at indicated temperatures (°C.).*

one-quarter of the combined water in the chrysotile molecule. This is in agreement with the data obtained by Warren and Bragg (8) who, as the result of X-ray studies, have proposed the formula $(OH)_6Mg_6Si_4O_{11} \cdot H_2O$, a structure that suggests that one-quarter of the water present is less firmly held than the remainder. The data indicate further that not more than about one-half of the combined water is driven off on prolonged heating at 510° C. Complete dehydration may possibly result on heating for very long periods at temperatures slightly above 516° C., but only when the fibre is heated at 704° C. will complete dehydration take place in less than one hour.

The minor inflections in the curves noted at temperatures of 400 to 450° C. (Figs. 1 and 3) seem to confirm an observation made by previous investigators

TABLE II

PERCENTAGE LOSS IN WEIGHT UPON HEATING A SAMPLE OF CANADIAN CHRYSOTILE ASBESTOS (MILL FIBRE) AT ALL TEMPERATURES AND PERIODS OF TIME (REPEATED HEATING)

Temp. of heating, °C.	Period of heating, hr.			
	0.50	1.5	3.5	21
555	4.58	5.05	5.75	10.55
582	10.55	11.17	11.47	13.33
604	13.73	13.51	13.53	13.84
632	13.95	13.97	14.10	14.11
671	14.12	14.13	14.14	14.29
704	14.30	14.33	14.32	14.43
904	14.78	14.85	14.80	15.01

(1, 2), who suggest that this may be due to the decomposition of brucite, present in the chrysotile as an impurity. There is, however, reasonable doubt regarding the validity of such a conclusion.

The results obtained by the repeated heating of the same sample of fibre are essentially the same as those of the single heating method, up to 555° C. Above this temperature and up to 704° C. (Table II) the loss in weight was different, as was to be expected from a consideration of the results in Table I. Comparable results for a heating period of 0.50 hr. are shown graphically in Fig. 4.

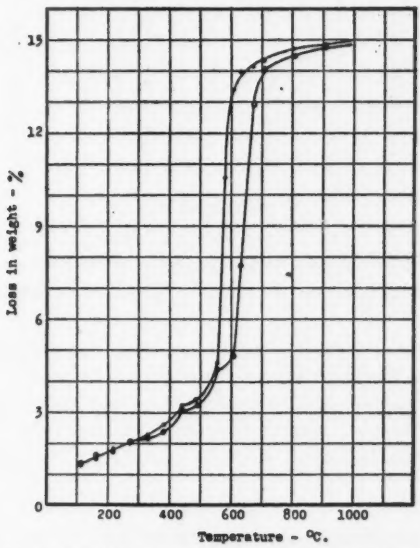

FIG. 4. *Weight lost by Canadian chrysotile asbestos (mill fibre) on heating for 0.50 hr. o Separate samples (i.e., single heating). • Same sample (i.e., repeated heating).*

The recovery of weight by the heated samples, when exposed in the conditioning room, is shown in Table III, in which the resorbed water is expressed as a percentage of the weight lost during heating. The results indicate that dehydration of the chrysostile molecule, that is, the loss of combined water, does not begin until the fibre has been heated at 216° C., for at least an hour. This would suggest that the present accepted method of determining sorbed moisture by drying to constant weight at 105 to 110° C.* gives low results. It would appear that a more accurate and more rapid procedure would be to dry for 0.50 hr. at approximately 215° C.

The amounts of water resorbed by the heated fibre, expressed as a percentage of the weight of the heated fibre, are given in Table IV, and graphically illustrated for the fibre heated for 0.25 hr. and 20 hr., in Fig. 5. These results

* *A.S.T.M. Standards on Textile Materials, 1939, page 50.*

TABLE III

PERCENTAGE RECOVERY OF WEIGHT LOST BY CANADIAN CHRYSOTILE ASBESTOS (MILL FIBRE) HEATED AT VARIOUS TEMPERATURES AND PERIODS

Temperature of heating, °C.	Period of heating, hr.				
	0.25	0.50	1	2	20
160		100	100	98	100
216	99	100	99	96	93
271	89	89	88	87	81
327	84	82	83	83	80
382	82	81	78	79	74
438	74	77	72	72	69
493	71	70	69	66	55
555	62	62	48	45	40
604	47	47	40	39	34
632	40	39	36	36	28
671	46	44	40	39	16
704	41	38	35	33	11
804	13	12	10	10	9
904	10	9	9	8	6

indicate that the observed loss in weight, caused by heating, is at the higher temperatures accompanied by chemical or physical changes, or by both, in the fibre.

The presence of the sorption maximum is of theoretical and possibly of practical interest. Haraldsen, as a result of his studies (3) concluded that serpentine decomposes to give olivine and silica, and that these products recombine at still higher temperatures to form enstatite. If such changes occur when serpentine is heated, it might reasonably be expected that similar

TABLE IV

PERCENTAGE WATER RESORBED BY CANADIAN CHRYSOTILE ASBESTOS (MILL FIBRE) AFTER HEATING AT VARIOUS TEMPERATURES AND PERIODS*

Temperature of heating, °C.	Period of heating, hr.				
	0.25	0.50	1	2	20
160		1.65	1.55	1.51	1.66
216	1.74	1.82	1.82	1.82	1.83
271	1.79	1.88	1.74	1.77	1.80
327	1.82	1.80	1.95	1.98	2.05
382	1.94	2.00	2.28	2.26	2.34
438	2.43	2.48	2.47	2.40	2.36
493	2.48	2.44	2.48	2.45	2.12
555	2.42	2.44	2.06	2.01	2.14
604	2.38	2.37	2.71	3.42	5.29
632	2.70	3.26	4.52	5.54	4.49
671	4.51	6.56	6.38	6.33	2.67
704	6.30	6.18	5.87	5.55	1.83
804	2.25	2.11	1.74	1.79	1.56
904	1.66	1.63	1.57	1.41	1.09

* *Calculated on basis of the weight after heating.*

reactions take place in the thermal decomposition of chrysotile. The sorption maxima observed may then be due to the transitory presence of silica, and not merely to surface effects.

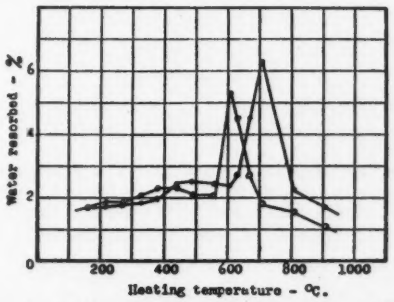

FIG. 5. *Resorption of water by Canadian chrysotile asbestos (mill fibre) after heating.* • *0.25 hr.* ○ *20 hr.*

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THERMAL STUDIES ON ASBESTOS

II. EFFECT OF HEAT ON THE BREAKING STRENGTH OF ASBESTOS TAPE AND GLASS FIBRE TAPE[1]

By D. Wolochow[2]

Abstract

The first result of heating pure chrysotile asbestos tape, crocidolite (blue) asbestos tape, and glass fibre tape to drive off the adsorbed moisture is an increase in breaking strength.

Pure chrysotile tape does not lose strength till a temperature of 370° C. is exceeded. Prolonged heating at 430° C. causes a loss in strength of about 20%, at 480° C. of about 40%. Heating at 540° C. causes a rapid loss in strength.

Crocidolite asbestos tape loses strength more rapidly than chrysotile asbestos tape.

Glass fibre tape, though initially stronger than chrysotile tape, is considerably less resistant to heat, beginning to lose strength rapidly at about 250° C., whereas chrysotile asbestos tape does not suffer any appreciable decrease in strength till a temperature of 400° C. is exceeded.

The literature (1, p. 56; 2; 3) contains little information on the effect of the temperature and the time of heating on the breaking strength of absestos textiles.

Most of the tests described below were made on pure (Grade AAAA) chrysotile asbestos tapes, but the results of some tests on underwriters' grade chrysotile asbestos, on crocidolite (blue) asbestos, and on glass fibre tapes are also reported.

Test Method

The samples were cut into 6-in. strips and conditioned at 65% relative humidity and 70° F. Twenty strips were taken for each test, in which the strips were heated in an electric furnace having automatic temperature control (±8° C.), cooled in a desiccator, and then broken in a standard pendulum type of testing machine. The loss in weight was also determined.

Test Results

The pure chrysotile asbestos tapes were all of the same nominal dimensions (1 in. wide and $\frac{1}{16}$in. thick), but because of various factors there were considerable differences in the breaking strength. These differences were of interest in another connection, but they do not affect the present study, which is primarily concerned with changes in breaking strength due to heating, rather than with actual breaking strengths. The breaking strength after heating was therefore in each case expressed as a percentage of the initial breaking strength, and the relative strengths were then averaged. These average relative breaking strengths have been plotted in Figs. 1, 2, and 3.

[1] *Manuscript received September 16, 1940.*

Contribution from Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 970.

[2] *Chemist.*

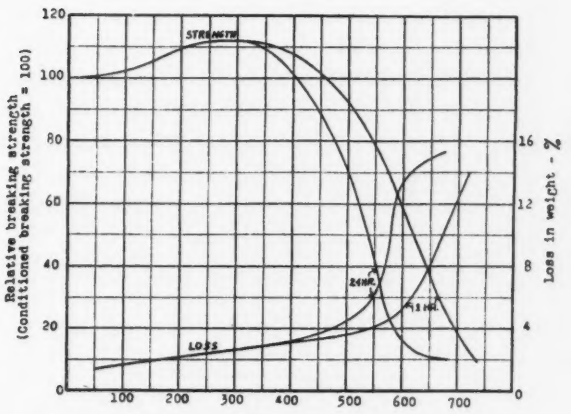


Fig. 1.

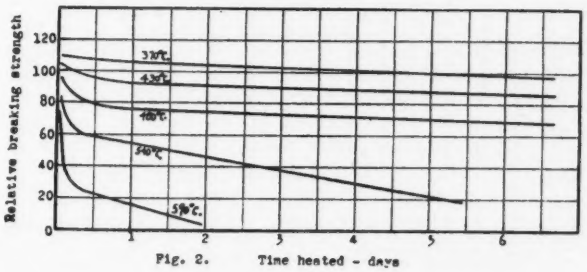


Fig. 2.

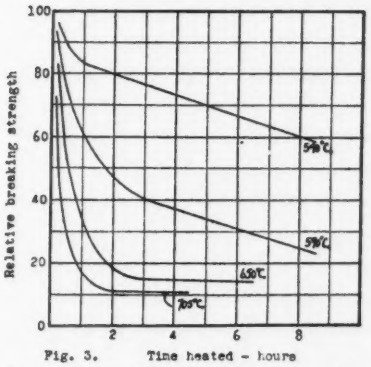
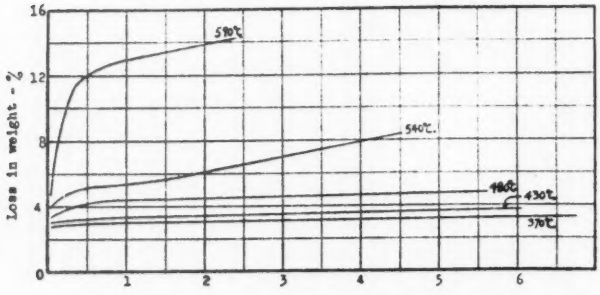


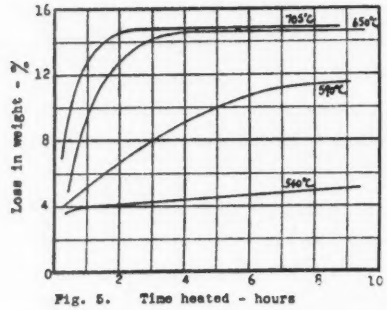
Fig. 3.

FIG. 1. *Relative breaking strength and loss in weight of pure chrysotile asbestos tape heated for 1 and 24-hr. periods.*

FIG. 2. *Relative breaking strength of pure chrysotile asbestos tape after prolonged heating at 370 to 590° C. (700 to 1100° F.).*

FIG. 3. *Relative breaking strength of pure chrysotile asbestos tape heated at 540 to 705° C.*





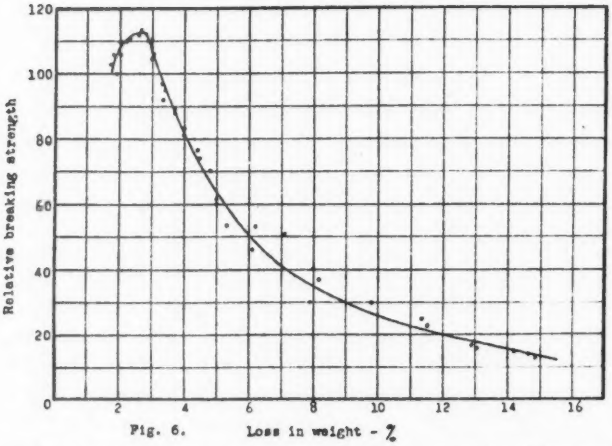


FIG. 4. *Loss in weight of pure chrysotile asbestos tape after prolonged heating at 370 to 590° C.*

FIG. 5. *Loss in weight of pure chrysotile asbestos tape heated at 540 to 705° C.*

FIG. 6. *Relation between relative breaking strength and loss in weight on heating.*

The weight losses were also averaged and the values have been plotted in Figs. 1, 4, and 5.

The relation between relative breaking strength after heating and loss in weight (average values for all pure chrysotile tapes tested) is shown in Fig. 6.

The extent of the variations in actual breaking strength and in the effect of heating, as illustrated by the curves for four samples of pure chrysotile tape, is shown in Fig. 7.

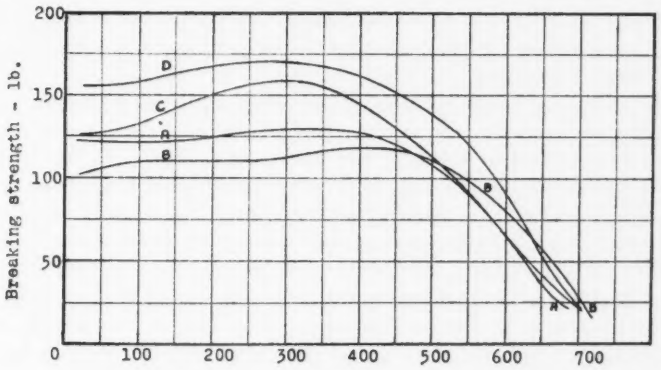


Fig. 7.

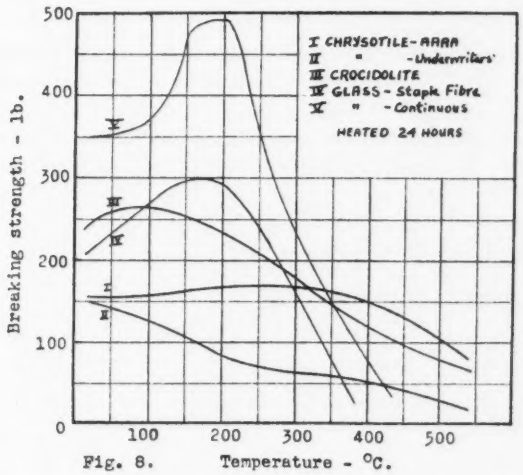


Fig. 8.

FIG. 7. *Variations in the breaking strength of pure chrysotile asbestos tapes heated one hour.*

FIG. 8. *Effect of heat on the breaking strength of chrysotile, crocidolite, and glass fibre tapes.*

The effects of heat on a pure chrysotile tape, an underwriters' grade tape, a crocidolite (blue) tape, and two glass fibre tapes, one made from the staple, the other from the continuous filament type of glass fibre, are shown in Fig. 8.

The maximum loss in weight of the crocidolite tape (0.0975 in. thick) was about 2%, of the staple fibre glass tape (0.015 in. thick) about 4%, and of the continuous filament glass tape (0.010 in. thick) about 4.5%.

Discussion of Results

The first noticeable effect of heating is an increase in the relative breaking strength of pure asbestos tape, amounting to an average of 12% at about 300° C., up to which temperature the effect of heating seems to be practically independent of the length of time the heating is continued. This increase in strength is most probably due to the removal of adsorbed moisture. If the heating is continued after the adsorbed moisture has been driven off, the tapes begin to lose strength, but the strength does not drop below the initial value, no matter how long the heating is continued, at any temperature below 370° C. Above this temperature, the strength begins to drop, decreasing to the initial value after one hour at 460° C. or after 24 hr. at 405° C. It is only above 480° C. that a rapid loss in breaking strength takes place.

It is evident that pure chrysotile asbestos tape retains its original breaking strength over a wide temperature range. Initially, the particular sample tested was not nearly as strong as the glass fibre tape (see Fig. 8), but after heating for 24 hr. at 400° C. it had retained all its initial breaking strength, whereas the glass fibre had retained only a fraction of its breaking strength and had only half the strength of the asbestos.

The crocidolite tape showed a small increase in breaking strength, followed by a decrease, which is much more rapid than in the case of the chrysotile asbestos.

The underwriters' grade of asbestos tape begins to lose strength as soon as heat is applied. This is of course due to the presence of cotton in the tape.

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PECTIC SUBSTANCES IN COTTON[1]

By Frank Leger[2] and P. Larose[3]

Abstract

The quantitative distribution of pectic substances* in raw cotton has been studied. A new method for the removal of cuticle pectin has been utilized.

A combination of this method with analysis for α-cellulose has shown that the non-cellulosic material in undamaged cotton appears to be present in the form of pectin.

In direct support of recent work carried out by Harris and co-workers (5, 6), and in contrast to that published by Farr (3), it has been found that reduction of pectin content from 1.18 to 0.12% resulted in a change of fluidity from 1.93 to 2.08, whereas treatment with hydrochloric acid raised the fluidity to 25.8.

It is suggested that there is no essential chemical difference between pectin in the cuticle surrounding the fibre and that distributed throughout the fibre.

Introduction

This paper reports results of work carried out during the past few months in connection with an investigation of the degradation of cellulose. Besides presenting some new facts, it corroborates recent work published by Whistler, Martin, and Harris.

It was felt that the method employed by Farr (3, 4) for the removal of pectic substances, viz., the use of hydrochloric acid solutions, was too drastic and resulted not only in the removal of pectin but also in a degradation of cellulose. This was shown to be the case by determinations of α-cellulose and of fluidities. Moreover, Harris (6) has pointed out that the method removes only a part of the original pectin.

There is considerable danger of degradation of cellulose in any method utilizing solutions of strong acids or bases for the removal of pectic material from cotton. With this in mind, it was thought that the use of a dilute solution of a mild base, such as sodium carbonate, would be preferable. That this assumption was justified is shown by the results that follow.

Methods

An American raw cotton was dewaxed by extraction in a Soxhlet with neutral chloroform for a 24 hr. period, followed by several extractions with boiling water. The residual cotton was then air dried.

[1] *Manuscript received in original form August 2, 1940, and as revised, September 22, 1940. Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 968.*

[2] *Research Assistant.*

[3] *Chemist.*

* *Pectin or pectic substance is used to designate those carbohydrate materials that contain galacturonic acid units, as determined by the rate of evolution of carbon dioxide on treatment with boiling 12.8% hydrochloric acid.*

In order to remove pectic material, this cotton was boiled for eight hours with an aqueous 1% solution of sodium carbonate (the ratio of cotton to solution was 1 : 30). A further similar extraction was carried out with fresh carbonate solution. During the first eight hour extraction, samples of cotton were removed at one hour intervals, acidified with 0.5% acetic acid, washed free of acid, and dried. These samples were used for a microscopic examination of fibres stained with a solution of ruthenium red and for the microscopic observation of their behaviour on treatment with cuprammonium solution. At the end of the eight hour treatment, the cuticle was apparently completely removed.

Since removal of pectin was not complete after the eight hour extraction, the cotton was further treated with a 0.5% aqueous solution of ammonium oxalate for eight hours at 75° C., followed by a 24 hr. extraction with the same solution at room temperature.

Isolation of the sodium-carbonate–soluble pectin was accomplished as follows: The carbonate solution was acidified with dilute hydrochloric acid (10%), whereupon a flocculent precipitate settled out. This was filtered off and washed with 95% ethanol. The residue was dissolved in a minimum quantity of 0.5% ammonium oxalate solution at 75° C., the solution was cooled to 10° C., acidified to pH 2.6, and to it was added two volumes of ethanol. The resulting gel was removed by filtration, dried under reduced pressure at 40° C., and purified by repeated solution in boiling water, cooling, and adding two volumes of ethanol. The final gel was dried as above.

The α-cellulose was determined by means of the standard method (2). Fluidities were determined in cuprammonium hydroxide solution containing 15 ± 0.1 gm. of copper, 200 ± 10 gm. of ammonia, and less than 0.5% of nitrite. The concentration of the cellulose in the cuprammonium solution was 0.5%. X Type B.C.I.R.A. viscometers were used for the fluidity measurements.

Pectin was determined from the rate of evolution of carbon dioxide on boiling a sample with 12.8% hydrochloric acid solution. The apparatus was that of Dickson, Otterson and Link (1) so modified as to permit its application to semi-micro determinations. A further change was made in that the evolved carbon dioxide was carried to the absorption tower in a stream of carbon-dioxide–free nitrogen instead of by the application of a vacuum. A barium hydroxide solution (0.02 N) was used in the absorption tower, and the excess of alkali was determined by back titration with hydrochloric acid (0.02 N). Phenolphthalein was used as an indicator and carbon-dioxide–free solutions were used throughout. A constant correction was applied for carbon dioxide evolved from the cellulose itself (6, 7). The value used was 0.45 mg. of carbon dioxide from 1 gm. of cellulose in 2.5 hr. At an oil bath temperature of 150° C., 2.5 hr. was found to be sufficient time for complete removal and absorption of pectin carbon dioxide, and was the time used in all these experiments. The pectin content was calculated by multiplying the amount of pectin carbon dioxide by 4.8 (6, 7).

TABLE I

CHANGE IN PECTIN CONTENT AND IN FLUIDITIES OF COTTON AFTER VARIOUS TREATMENTS

Sample No.	1	2	3	4
α-cellulose, %	99.0	99.1	99.5	99.7
Pectin in α-cellulose, %	0.21	0.21	0.10	0.07
Pectin, % of whole fibre	1.18	0.99	0.30	0.12
Fluidity, rhes.	1.93	2.03	2.00	2.08

Sample 1—dewaxed cotton.
Sample 2—as for Sample 1, extracted with aqueous sodium carbonate (1.0%) at 100° C. for eight hours.
Sample 3—as for Sample 2, extracted with ammonium oxalate (0.5%) at 75° C. for eight hours.
Sample 4—as for Sample 3, extracted with the same ammonium oxalate 24 hr. at 25° C.

Discussion of Results

Table I summarizes some of the results obtained.

A microscopic examination of Sample 2, stained with ruthenium red and dissolved in cuprammonium hydroxide, indicated that the cuticle had been entirely removed after the eight hour treatment with 1.0% sodium carbonate solution. Complete removal of the cuticle resulted in a loss of only 16% of the pectin originally present in the cotton, as shown by a comparison of the results obtained with Samples 1 and 2.

However, the results given in Table II, show that further treatment with 1% sodium carbonate solution extracts more pectin, until at the end of 24 hr. practically all the pectin has been removed. It would thus seem that there is no essential chemical difference in cuticle and fibre pectin, although the latter is removed more slowly, probably owing to the slow rate of diffusion of the sodium carbonate solution into the fibre. Since complete removal of the cuticle results in elimination of only 16% of the pectin, corresponding to 0.2% of the dewaxed cotton, this would represent a maximum value for the cuticle pectin.

TABLE II

EFFECT OF TIME OF EXTRACTION BY SODIUM CARBONATE SOLUTION ON PECTIN CONTENT OF COTTON

Sample	Original	1	2
Pectin, % of whole fibre	1.18	0.17	0.17

Original—dewaxed cotton.
1—original extracted for 24 hr. at 100° C. with 1% sodium carbonate.
2—As for Sample 1, but extracted for 48 hr.

The amounts of pectin originally present in the dewaxed cotton and in the cotton practically free of pectin are in complete agreement with those found by Whistler, Martin, and Harris (5).

The material recovered from the sodium carbonate solution by the method outlined in the section on methods had a pectin content of 69.8%, which corresponds closely to that of a commercial pectin.

Fluidity determinations of cuprammonium hydroxide solutions of cotton extracted with sodium carbonate and with ammonium oxalate solutions at various stages of pectin removal, have been carried out, and the results are given in Table I. These show that the fluidity does not depend on pectin content.

In Table I are also included the results of the determination of α-cellulose in the cotton at various stages of pectin removal. These results indicate a close agreement between the α-cellulose content and total non-pectin material in the fibre. This holds only when there is no degradation as shown by the fluidity values. Some of the original cotton was treated for 0.5 hr. according to Farr's method for the removal of pectin (3, 4), and the resulting cotton tested for α-cellulose and fluidity. The results are given in Table III.

TABLE III

EFFECT OF TREATMENT WITH HYDROCHLORIC ACID ON α-CELLULOSE CONTENT AND FLUIDITY OF COTTON

Sample	Original	Treated
α-cellulose, %	99.0	91.4
Fluidity, rhes.	1.93	25.8

Original—dewaxed cotton.
Treated—Original, treated 30 min. at 25° C. with hydrochloric acid (sp. gr. = 1.18).

The change in α-cellulose content from 99.0 to 91.4% definitely indicates that degradation has taken place, and it is reasonable to conclude, therefore, that the change in fluidity is due to this degradation and not to the removal of pectin. This substantiates recent work by Harris (5), in which it is shown that treatment of cotton with concentrated hydrochloric acid removes only a small part of the pectin present. From the foregoing, an α-cellulose content of less than 98.5% would indicate possible degradation of the cotton, with correspondingly higher fluidity values.

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